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THE STRUCTURE OF LB DEPOSITED FILMS OF DIACETYLENES. David Johnson<sup>(b)</sup>,  
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We have examined the structure of various diacetylene monolayers and multilayers deposited by the Langmuir Blodgett technique or one of its variations. Various experimental techniques were used including x-ray diffraction, electron diffraction (ED), and scanning force microscopy (SFM). In particular salts of the monomers  $\text{CH}_3-(\text{CH}_2)_n-\text{C}\equiv\text{C}-(\text{CH}_2)_m-\text{COOH}$  were deposited and polymerized by exposure to UV light. The purpose of this paper is to compare the information obtained by these three tools for determining structure of LB films. Monomer unit mesh: SFM;  $a=0.51\pm0.04$  nm,  $b=0.88\pm0.06$  nm, rectangular centered net. ED;  $a=0.483$  nm,  $b=0.92$  nm, rectangular net 2-D, orthorhombic 3-D lattice. The area per molecule is  $0.224$  nm<sup>2</sup> and  $0.222$  nm<sup>2</sup> per molecule respectively. Polymer unit mesh: Here there is a discrepancy between the SFM and ED data. SFM;  $a=0.466\pm0.008$ nm,  $b=0.55\pm0.01$ nm  $\theta=100\pm2$  deg., oblique net mesh area =  $0.252$  nm<sup>2</sup>/molecule. ED;  $a=0.489$ nm,  $b=0.811$  nm, rectangular net mesh area =  $0.198$  nm<sup>2</sup>/molecule. These data will be discussed

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# THE STRUCTURE OF LB DEPOSITED FILMS OF DIACETYLENES

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## Introduction

In a series of papers [1-5] we have examined the structure of various diacetylene monolayers and multilayers deposited by the Langmuir Blodgett technique or one of its variations. Various experimental techniques were used including x-ray diffraction, electron diffraction and scanning force microscopy (SFM). In particular salts of the monomers  $\text{CH}_3-(\text{CH}_2)_n-\text{C}\equiv\text{C}-(\text{CH}_2)_m-\text{COOH}$  (designated as n-mAC) were deposited and polymerized by exposure to UV light. There are strong geometric constraints that must be met for substantial conversion to occur [3]. Moreover, while the monolayers formed at the air/water interface are solids (the monolayer compressibility is small), after polymerization the films are rigid. It was possible to transfer bilayers of the polymerized lithium salt of 16-8 AC so as to span the openings in grids suitable for electron diffraction [3]. The cadmium salt of 12-8 AC can be deposited by the Langmuir Blodgett technique to form multilayers of sufficient thickness to allow x-ray diffraction spots to be collected for analysis [4, 6]. In a separate series of experiments [1,2] multilayers of the Cadmium salt of 12-8AC were deposited on glass microscope slides as steps and analyzed by scanning force microscopy (SFM). We remark that of the techniques only SFM does not cause polymerization of m-nAC by radiation used to determine structure.

The purpose of this paper is to compare the information obtained by these three tools for determining structure of LB deposited m-n AC.

## Experimental

The techniques of Lanmuir Blodgett deposition is described in many places [7] including our own publications [1-6]. Modified Lauda troughs were used for the depositions which were done in a class 100

clean room. Pure water was used that passed the shake test for surfactant residue; Lithium or Cadmium salts were added to the substrates. Electron diffraction of 16-8AC salts was accomplished by deposition of bilayers on grids [3]. X-ray diffraction was done on multilayers deposited on glass substrates. SFM was done on LB films deposited on smooth glass substrates. A Digital Instruments Nanoscope III was used to image the films using pyramidal silicon nitride tips. Scans were done with forces below 5nN and care was taken to test for artifacts due to the contact mode of operation [1,2]. Consult the original papers for details. We remark that the electron diffraction data set for the polymer included 13 independent reflections and did not produce a unique structure; the most probable structure was reported. SFM was done over areas that varied between 70 by 70 nm<sup>2</sup> and 5 by 5 nm<sup>2</sup>. The numbers quoted herein were done by direct and Fourier transform analysis on image areas of 16 by 16 nm<sup>2</sup>. The domains could be observed at larger areas.

## Results

None of the techniques alone provided enough data to determine the three-dimensional structure of the LB unit cell; we limit the discussion here to the two-dimensional net. The results are given first for the monomer. Monomer unit mesh:

Ref.2(SFM);  $a = 0.51 \pm 0.04$  nm,  $b = 0.88 \pm 0.06$  nm, rectangular centered net.

Ref.3;  $a = 0.483$  nm,  $b = 0.92$  nm, rectangular net 2-D, orthorhombic 3-D lattice.

Both structures have two molecules per unit mesh. The area per molecule is 0.224 nm<sup>2</sup> and 0.222 nm<sup>2</sup> per molecule respectively. The area per molecule at deposition (30mN/m) was about 0.21nm<sup>2</sup> per molecule. To complete the picture of the 3-dimension cell, the (d-spacing)/2 was determined to be 2.87 nm by SFM and 2.80nm by x-ray reflectivity [4]. We believe that these numbers are consistent and accurate.

Polymer unit mesh: Here there is a discrepancy between the SFM and diffraction data.

Ref.[2] (SFM);  $a = 0.466 \pm 0.008$ nm,  $b = 0.55 \pm 0.01$ nm  $\theta = 100 \pm 2$  deg., oblique net, in 2-D, mesh area = 0.252 nm<sup>2</sup>/molecule.

Ref.[3];  $a = 0.489$ nm,  $b = 0.811$  nm, rectangular net mesh area = 0.198 nm<sup>2</sup>/molecule.

## Discussion

It is clear that the monomer data are consistent between the SFM and electron diffraction methods. This result strongly supports the SFM methodology reported in [1] and especially [2] for obtaining structure of the net with few artifacts. The error bars on the SFM data represent averaging over at least five different locations on each sample and at each location at least 11 images using various scan protocols including a range of forces. However, even at forces of 5nN or less there is no doubt that the tip is plowing into the soft-matter of the film. Apparently the tip is not penetrating more than a few  $\text{CH}_2$  groups. In fact there is a "hard core" beyond which the penetration force is substantial and larger than 5nN. It seems likely that the SFM images are of that region of the top layer molecules of the LB films. Keeping in mind the good correlation found for the unpolymerized 12-8 AC it was then a surprise to measure a significantly larger net for the polymerized LB film. The color change observed during polymerization is an indicator that good conversion was obtained. Moreover, the d-spacing contracted as expected but the mesh area expanded in the SFM determination. We believe that the SFM data is reflecting a structure change due to polymerization but it is not accurately portraying a single crystal of the polymer. While artifacts cannot be ruled out, the monomer data suggests that SFM is reporting a real structure of the surface ( $\text{CH}_2$ ) groups only slightly perturbed by the scan process. We expect to repeat these measurements using both contact mode and tapping mode.

The diffraction results for the polymer are reasonable although the mesh area may be slightly small approaching that of a single crystal, straight chain acid. However the e-beam damage was substantial. The weak reflections persisted only for 15s after the start of exposure and the strong reflections remained for two minutes. Electron and x-ray diffraction sample the entire unit cell of an LB film and in principle are capable of determining accurately atom positions. Even so the fact that damaging radiation is not used in SFM make that technique useful for structure studies of LB films. This work was supported by ALCOM under the NSF grant number DMR-8920147 and ONR grant number N00014-94-1-01270.

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8. We are sad to report the passing of Professor Johnson in Dec. 1995. Correspondence should be directed to Lando or Mann.